(54) Extruded stretched filament of ultra-high-molecular-weight polyethylene and production method and apparatus thereof.

(73) Proprietor: MITSUI PETROCHEMICAL INDUS-
TRIES, LTD.
2-5, Kasumigaseki 3-chome Chiyoda-ku
Tokyo 100(JP)

(72) Inventor: Shiraki, Takeshi
2-7, Waki 5-chome Waki-cho
Kuga-gun Yamaguchi(JP)
Inventor: Yoshimura, Yoshihiro
13-13, Imazu-cho 4-chome
Iwakuni-shi Yamaguchi(JP)
Inventor: Nakashima, Koji
Kamihama Shinkai 8774-188 Ohno-cho
Saiki-gun Hiroshima(JP)

(74) Representative: Geering, Keith Edwin et al
REDDIE & GROSE 16 Theobalds Road
London WC1X 8PL(GB)

Description

The present invention relates to an extruded stretched filament of ultra-high-molecular-weight polyethylene and to a method and apparatus for producing the same.

5   Ultra-high-molecular-weight polyethylene is increasingly used as a so-called engineering plastic because of its excellent impact resistance, abrasion resistance, chemical resistance, tensile strength, and other properties, when compared with conventional polyethylene. However, ultra-high-molecular-weight polyethylene has an extremely high melt viscosity and poor flowability when compared with conventional polyethylene, and thus it is very difficult to mold such a plastic by conventional extrusion molding and

10   injection molding. Accordingly, ultra-high-molecular-weight polyethylene is generally molded by compression molding; with the exception of rods and the like, which are partly extrusion molded at a very low extrusion speed.

On the other hand, as a method for stretching the monofilament of high-density polyethylene at a high draw ratio, it has been proposed in, for example, Japanese Examined Patent Publication (Kokoku) No. 37-

15   9765, that an additive (e.g., o-chlorobenzene, xylene) having a boiling point higher than the melting point of the polyethylene is incorporated into the polyethylene in an amount of 20% to 150% by weight based on the weight of the polyethylene and the resultant dispersion is formed into a primary fibrous material, followed by hot stretching at a draw ratio of 3 to 15 while retaining the 5% to 25% by weight corresponding amount of the additive in the spun threads. It has been also proposed in, for example, Japanese

20   Unexamined Patent Publication No. 56-15408, that a solution of linear polyethylene having a molecular weight of 400,000 or more is spun, followed by stretching the same at a temperature such that the modulus of at least 20 GPa can be obtained. However, although these methods can provide stretched filaments having a high elasticity and high strength, raw filaments having a diameter of more than 1 mm⌀ are very difficult to obtain since a solution having an extremely low viscosity obtained by diluting ultra-high-

25   molecular-weight polyethylene with a large amount of a solvent is extruded and processed. Thus, the stretched thread has a diameter of at most about 0.042 mm⌀ (50 deniers) and generally of 0.038 mm⌀ (10 deniers) or less.

Accordingly, since a large amount of these stretched fine threads must be intertwined to form thick ropes and nets having a high strength, or cords for cord cutters (i.e., lawn mowers), there are problems in

30   that the process operations are troublesome, the stiffness of the resultant ropes and nets is unpreferably high, and the flexibility is insufficient. Furthermore, the resultant ropes and nets are usually very hairy.

In addition, it has been proposed in, for example, Japanese Unexamined Patent Publication (Kokai) No. 52-74682, that polymers having a weight-average molecular weight of 150,000 or more are processed under the conditions of a temperature of about 75°C to about 140°C and a deformation ratio of about 18 or more

35   to form elongated and orientated polymers. However, this reference describes that the diameter of fibers or the thickness of films or tapes before stretching is preferably about 1 mm or less. Also, the Examples given therein only disclose that polyethylene having a molecular weight of about 300,000 is spun through circular orifices having a diameter of 1 mm to form thin filaments having a diameter of 0.7 mm or less and, in the case of polyethylene having a molecular weight of 800,000, filaments are prepared only by stretching

40   dumbbell-shaped samples having a gauge dimension of 1 cm x 0.2 cm derived from the compressed sheet having a thickness of 0.5 mm. Thus, it has not been established in the art that filaments having a diameter of more than 1 mm⌀ can be industrially produced from ultra-high-molecular-weight polyethylene having an extremely high molecular weight.

Furthermore, it has been desired in the art to substitute plastic wires for the iron wires usually used in,

45   for example, orchards, e.g., for tying the loculi of fruit and for grape-vine trellises, because iron wires easily rust and cannot withstand the effects of long-term use. However, conventionally commercialized plastic wires composed of nylon and polypropylene have a certain elasticity and, therefore, cannot be plastically deformed, unlike iron wires: For example, plastic wires cannot be firmly joined only by twisting.

The present invention addresses disadvantages of the prior art and provides for production of an

50   extruded filament of ultra-high-molecular-weight polyethylene having an outer diameter of 0.2 to 20 mm, e.g. more than 1-mm⌀, and a stretched such filament.

In accordance with the present invention, there is provided an extruded stretched filament of ultra-high-molecular-weight polyethylene having an intrinsic viscosity [π] of at least 3.5 dl/g as determined in decalin solvent at 135°C, a tensile strength at break of at least 98.0665 MPa (10 kg/mm²), a draw ratio of at least 3,

55   a C axis orientation degree of at least 0.9, and an outer diameter of 0.1 to 10 mm⌀.

In accordance with the present invention, there is also provided a method for producing an extruded filament of ultra-high-molecular-weight polyethylene comprising the steps of:
melting the ultra-high-molecular-weight polyethylene in a screw extruder;

extruding the molten ultra-high-molecular-weight polyethylene from a die having an L/D ratio of at least 10 and an S_1/S_2 ratio of 1.0 to 5.0 where S_1 and S_2 are the respective cross-sectional areas of the inlet and outlet portions of the die; and

taking-off the extrudate at a draft ratio of at least 1 while the extruded strands are gradually cooled.

In accordance with the present invention, there is further provided an apparatus for producing an extruded

filament of ultra-high-molecular-weight polyethylene comprising, in sequence in the machine direction.

an extruder provided with a grooved cylinder and a screw having a compression ratio of 1 to 2.5;

a die connected to the screw tip, said die having an L/D ratio of at least 10 and S_1/S_2 ratio of 1.0 to 5.0 where S_1 and S_2 are the respective cross-sectional areas of the inlet and outlet portions of the die;

a gradual-cooling cylinder provided with an air ring or a sizing die at the inlet portion thereof for the extruded strand; and

a taking-off unit.

The present invention will be better understood from the description set forth below with reference to the accompanying drawings, wherein:

Fig. 1 schematically illustrates a cross-section of a typical embodiment of an apparatus for producing a stretched filament of ultra-high-molecular-weight polyethylene according to the present invention;

Figs. 2(a) and (b) schematically illustrate the conditions of the plastic wire 21 according to the present invention when the plastic wire 21 is folded; and

Figs. 3(a) and (b) schematically illustrate the conditions of the plastic wire 22 according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The ultra-high-molecular-weight polyethylenes usable in the present invention are crystalline ethylene homopolymer or crystalline ethylene-alpha-olefin copolymers having a major content of ethylene (e.g., an ethylene content of about 95 to about 100 mol%) having an intrinsic viscosity [η], determined at 135°C in a decalin solvent, of 3.5 dl/g or more, preferably 4 dl/g or more, more preferably 8 to 25 dl/g, and a melt flow rate (MFR), determined according to an ASTM D-1238(F) method, of 0.01 g/10 min or less. Examples of the alpha-olefin comonomers are those having 3 to 20 carbon atoms such as propylene, 1-butene, 1-hexene, 1-octene, and 4-methyl-1-pentene.

According to the present invention, the stretched filaments of ultra-high-molecular-weight polyethylene can be obtained by stretching raw filaments thereof prepared as mentioned below. The resultant stretched filaments have an intrinsic viscosity [η] of at least 3.5 dl/g, preferably 4 dl/g or more, more preferably 6 to 20 dl/g. a tensile strength (TS) at break of at least 98.0665 MPa (10 kg/mm^2), preferably 196.133 MPa (20 kg/mm^2) or more, more preferably 392.266 MPa (40 kg/mm^2)

or more, a draw ratio of at least 3, preferably 6 or more, a C axis orientation degree of at least 0.9, preferably 0.95 or more, and an outer diameter of 0.1 to 10 mm⌀, preferably 0.2 to 3 mm⌀. The length of the stretched filaments according to the present invention is substantially indefinite.

When the intrinsic viscosity [η] is less than 3.5 dl/g, the average chain length of the molecules is short and, therefore, the tensile strength is disadvantageously small even in the case of the higher draw ratio. When the TS at break is less than 98.0665 MPa (10 kg/mm^2),

sufficient strength cannot be obtained especially for use as ropes, nets or cords for a cord cutter. When the draw ratio is less than 3, stretched filaments having a TS of 98.0665 MPa (10 kg/mm^2)

or more are very difficult to obtain. When the C axis orientation degree is less than 0.9, not only are stretched filaments having a TS of 98.0665 MPa (10 kg/mm^2)

or more very difficult to obtain, but also the creep deformation (or elongation) of the product tends to become large.

When the outer diameter of the stretched filaments according to the present invention is less than 0.1 mm⌀, the productivity of the raw filament is low and is not practical, although the filament can be technically produced. Contrary to this, when the outer diameter is more than 10 mm⌀, the initial investment for the stretching device becomes unpreferably large and practical usage of the filament is poor.

According to the present invention, the raw filaments of the stretched filaments of the ultra-high-molecular-weight can be produced by melting the above-mentioned ultra-high-molecular-weight polyethyl-ene in a screw extruder, preferably a screw extruder provided with a grooved cylinder (or barrel), and then melt-extruding the molten polyethylene from a die having an L/D of at least 10, preferably 15 or more, more preferably, 30 to 60. After the extruding, the extrudate is taken-off at a draft ratio of at least 1, preferably 1.2 to 30, while the extruded strands are gradually cooled, preferably by passing through a cooling cylinder

3

having a length of, for example, 0.3 to 5 m, and air blowing at 15°C to 80°C. Thus, the desired raw filaments of ultra-high-molecular-weight polyethylene having an outer diameter of generally 0.2 to 20 mmⵁ, preferably 2 to 10 mmⵁ, and having an excellent stretchability can be obtained. The term. "draft ratio" used herein denotes the ratio of the take-off speed of the taking-off unit to the extruding speed of the extruded

5 polyethylene at the outlet of the die.

When a die having an L/D of less than 10 is used, the molten polyethylene has a poor melt flowability and is not completely uniformly fused before being extruded from the die, since the molten ultra-high-molecular-weight polyethylene is a rubber-like mass unlike the molten product of conventional polyethylene and, therefore, only raw filaments having a poor stretchability can be obtained. As a result, the stretched

10 filaments having sufficient strength cannot be obtained even after stretching. On the other hand, although there is no critical limitation to the upper limit of the L/D ratio, the preferable upper limit of the L/D ratio is 100 from a practical viewpoint. The shape of the die is generally circular or cylindrical. There is a correlationship between the productivity and the L/D ratio of the die. Thus, the larger the L/D ratio, the bigger the increase in the production rate (i.e., the taking-off speed).

15 When the molten strands extruded from the die are quenched, for example, by means of a water-circulation water bath, raw filaments having poor stretchability are obtained because bubbles having a vacuum are generated. in the cores of the strands and because the crystallinity becomes low. In addition, in order to obtain stretched filaments having an excellent tensile strength at break from the raw filaments obtained by the draft ratio of less than 1, the draw ratio must be at least 4 and thus loses efficiency.

20 According to the present invention, there are no critical limitations to the extrusion molding temperature of the ultra-high-molecular-weight polyethylene, as long as the temperature is higher than the melting point of the polyethylene but lower than the decomposition temperature thereof. The preferable extrusion temperature conditions of the above-mentioned ultra-high-molecular-weight polyethylene are an extruder temperature of 180°C to 350°C, a temperature between the inlet and the intermediate portion of the tube die of 180°C to 300°C, and temperatures between the intermediate portion and the outlet of the tube die of

25 135°C to 160°C. Thus, according to the present invention, the desired raw filaments of the ultra-high-molecular-weight polyethylene having an outer diameter of 0.2 to 20 mmⵁ, preferably 2 to 10 mmⵁ, especially when the wires are produced therefrom, can be obtained.

When the extruded raw filaments of the ultra-high-molecular-weight polyethylene having an outer

30 diameter of 0.2 to 20 mmⵁ are produced, either dry stretching or wet stretching may be carried out. However, the use of wet stretching is preferable from the standpoint of heat transfer efficiency and temperature control accuracy. Furthermore, the use of multiple-step stretching is preferable, when compared to single step stretching, because the draw ratio can be increased and because stretched filaments having a high strength can be obtained.

35 A typical embodiment of the apparatus suitable for use in the production of extruded raw filaments from the above-mentioned ultra-high-molecular-weight polyethylene will be explained in detail with reference to the accompanying drawing.

As illustrated in Fig. 1, the apparatus for producing raw filaments from the ultra-high-molecular-weight polyethylene comprises, in sequence from the extruder side, an extruder 1 provided with a grooved cylinder

40 2 and a screw 3 having a compression ratio of 1 to 2.5, preferably 1.3 to 1,8; a cylindrical die 6 connected to the tip of the screw 3, a cooling cylinder 9, and a taking-off unit 10. The die 6 has an L/D ratio of at least 10, preferably 15 or more, more preferably 30 to 60, and a ratio S_1/S_2 of a cross-sectional area S_1 of the inlet portion 4 of the die 6 to a cross-sectional area S_2 of the outlet portion 5 of the die 6 of 1 to 5, preferably 1.5 to 3.0. The cooling cylinder 9 for gradually cooling the extruded strands is provided with an

45 air ring or sizing die (not shown) at the inlet portion 8 of the strands.

The grooved cylinder 2 is provided with groove portions 11 to ensure a stable feed of the powder particles of the ultra-high-molecular-weight polyethylene to a compression zone 12. As mentioned above, the compression ratio of the screw 3 should be within the range of 1 to 2.5. When the compression ratio of the screw 3 is less than 1.0, the contact stress of the polyethylene against the cylinder wall is small, so that

50 the extrusion amount becomes unstable and the resultant extruded filaments will have a poor appearance due to surging or insufficient deaeration. Contrary to this, when the compression ratio of the screw 3 is more than 2.5, the polyethylene temperature is abnormally increased due to clogging and the generation of frictional heat in the compression zone, so that the friction coefficient and abrasion resistance of the extruded raw filaments are impaired due to a decrease in the molecular weight of the polyethylene caused

55 by thermal decomposition.

The term "compression ratio" of the screw 3 used herein is defined by a ratio of the groove depth at the hopper portion of the screw 3 to the groove depth at the screw tip.

The L/D ratio of the extruder 1 according to the present invention is generally 7 to 32, preferably 20 to

26. When the L/D ratio of the extruder 1 is less than 7, powder of the ultra-high-molecular-weight polyethylene is likely to be fed to the cylindrical die 4 because of incomplete melting.

On the other hand, when the L/D ratio of the cylindrical die 6 is less than 10, raw filaments having a poor stretchability are formed because the molten product of the ultra-high-molecular-weight is not completely fused before the molten product is extruded from the die. The L/D ratio of the cylindrical die 6 is defined by a ratio of the length L between the inlet portion 4 of the cylindrical die 6 and the outlet portion 5 of the die 6 to the inner diameter D of the die outlet 5. Also, as mentioned above, the ratio S_1/S_2 should be within the range of 1 to 5. When the ratio S_1/S_2 is less than 1, the fusion of the molten ultra-high-molecular-weight polyethylene becomes incomplete due to an insufficient inner pressure and, therefore, the appearance (or shape) of the extruded strand is worsened and the desired raw filaments having an excellent stretchability cannot be obtained. Contrary to this, when the ratio S_1/S_2 is more than 5, a so-called shear failure stream is possibly generated in the molten product and, therefore, an unpreferable low speed extrusion must be carried out.

There are no critical limitations to the length of the gradual-cooling cylinder 9 as long as the length thereof is sufficient to cool the molten strands extruded from the cylindrical die without quenching. For example, the length of the cooling cylinder 9 is generally 0.3 to 5 m, preferably 1 to 3 m. When the length of the cooling cylinder 9 is less than 0.3 m, the molten strands cannot be properly gradually cooled when the taking-off speed is high. The air ring provided at the inlet portion of the cooling cylinder 9 for molten strands is designed to gradually cool the molten strands by supplying warm air having a temperature off from 15°C to 80°C, preferably, 30°C to 50°C. Furthermore, in the apparatus according to the present invention, a sizing die (not shown) is optionally provided at the inlet side of the cooling cylinder 9 to control the size of the molten strands and to gradually cool those strands.

According to the present invention, the extruded strands having an intrinsic viscosity [η] of, for example, 4 dl/g, preferably 8 to 30 dl/g, and a TS at break of 196.133 MPa (20 kg/mm²) or more, preferably 490.3325 MPa (50 kg/mm²)or more, are stretched at a draw ratio of 8 to 30 to form whitened plastic wires. The resultant plastic wires of the ultra-high-molecular-weight polyethylene are oriented and crystallized in the stretching direction by stretching. As a result, the wires are divided into fine fibers to form whitened wires, and accordingly, when the wires are bent or twisted, deformation is caused by slip between the fibers based on stress. Thus, even after the stress is removed, such deformation can not be recovered and the wires brought to their original linear shape, due to the elasticity thereof.

The folding return angles θ when the present wire is folded at 90° and 180° are 20° or less, preferably 10° or less. The term "folding return angle" used herein means the returning angle θ after the wires are allowed to stand for 10 minutes at the folding conditions as shown in Figs. 2 and 3.

When the intrinsic viscosity [η] is less than 4 dl/g, the average molecular chain lengths are small and, therefore, the tensile strength cannot be increased even when the draw ratio is increased. On the other hand, when the TS at break is less than 196.133 MPa (20 kg/mm²), the strength is likely to be insufficient for enabling the plastic wires to be used instead of iron wires.

The outer diameter of the plastic wires according to the present invention is generally about 0.4 to 3.5 mmØ, preferably about 0.5 to 2.5 mmØ. The plastic wires according to the present invention can be used either as a single wire or as thicker wires obtained by twisting a plurality of single wires. When the outer diameter is less than 0.4 mmØ, the productivity of the raw filaments is low from the industrial point of view. On the other hand, when the thickness of the wire is more than 3.5 mmØ, the initial cost for the stretching apparatus is unpreferably large and also no practical use thereof can be expected.

The stretching temperature is preferably a temperature of the melting point of the ultra-high-molecular-weight polyethylene plus 15°C or less, preferably 80°C to 150°C, more preferably 100°C to 150°C. Although the stretching can be effected even at a temperature higher than the melting point of the ultra-high-molecular-weight polyethylene plus 15°C, the desired whitened wires having a high strength cannot always be obtained. Contrary to this, when the stretching temperature is too low, the desired high strength cannot always be obtained although the whitened wires can be obtained.

Although the stretching can be carried out at a single stage, a multi-stage stretching can be advantageously utilized because the draw ratio can be increased and because the desired stretched filaments having a high strength can be obtained.

The typical multi-stage stretching conditions are as follows. That is, the raw filaments or strands are stretched at a draw ratio of 4 to 8 at 80°C to 135°C in the first-stage, and the stretched filaments are then stretched at a draw ratio of 2 to 5 at 140°C to 150°C in the second-stage. Thus, the raw filaments are stretched at a total draw ratio of 8 to 30, preferably 10 to 30. The plastic wires thus obtained are oriented and crystallized in the stretching direction and are whitened.

As explained above, although the stretched filaments of the ultra-high-molecular-weight polyethylene

5

according to the present invention have an outer diameter of 0.1 to 10 mmø, which is very much thicker than that of conventional melt-spun filaments or the like of ultra-high-molecular-weight, the stretched filaments according to the present invention have an extremely high tensile strength at break, when compared to conventional stretched filaments of ultra-high-molecular-weight polyethylene, while retaining the inherent characteristics of the ultra-high-molecular-weight polyethylene such as abrasion resistance, self-lubricating properties, and impact resistance. Accordingly, the present stretched filaments can be advantageously used as, for example, thick ropes and nets for ship mooring and load carriers or cords for cord cutters (i.e., lawn mowers), for which the use of conventional ultra-high-molecular-weight polyethylene filaments is limited.

Furthermore, the above-mentioned production process and apparatus according to the present invention, can stably produce raw filaments of the ultra-high-molecular-weight polyethylene having an excellent stretchability, which filaments are suitable for producing stretched filaments having the above-mentioned characteristics and which have been difficult to produce heretofore.

Furthermore, as mentioned above, since the plastic wires produced according to the present invention are plastically deformable, these plastic wires can be twisted for tying in the same way as iron wires. Accordingly, the plastic wires according to the present invention can be substituted for conventional iron wires in any usage where no substantial heat is applied. For example, the plastic wires according to the present invention can be used for tying the loculi of fruit and for constructing grape-vine trellises and orchard shelves. In addition, since the plastic wires according to the present invention do not rust, unlike iron wires, the present plastic wires have an excellent serviceability and can be repeatedly used, without snapping the wires, due to the plastic deformability thereof.

EXAMPLES

The present invention will now be further illustrated by the following Examples.

Example 1 and Comparative Example 1

Stretchable raw filaments (or strands) of ultra-high-molecular-weight polyethylene were produced by using an apparatus for producing such stretchable raw filaments (or strands).

The specifications of the apparatus used are as follows.

Screw:　Outer diameter = 20 mmø
　　　　Effective screw length (L/D) = 22
　　　　Compression ratio = 1.8

Die:　　Length = 240 mm
　　　　Inner diameter at die outlet = 6 mmø
　　　　Die L/D = 40
　　　　S_1/S_2 = 1.8

Powdered ultra-high-molecular-weight polyethylene; Hizex® Million 240M (available from Mitsui Petrochemical Industries, Ltd. having an intrinsic viscosity $[\eta]$ of 16.5 dl/g, an MFR of less than 0.01 g/10 min, a melting point of 136°C, and a bulk density of 0.45 g/cm^3) was extruded from the above-specified extruder under the following conditions to produce stretchable raw filaments or strands of the ultra-high-molecular-weight polyethylene having an outer diameter of 4.0 mmø.

Setting temperature
　　Extruder = 320°C
　　Die base (D_1) = 200°C
　　Die tip (D_2) = 140°C
Screw revolution number = 50 rpm
Taking-off speed = 1.5 m/min.

The resultant strands were stretched in a stretching bath containing triethylene glycol at a draw ratio of 18 (i.e., first stage: 6 times at 133°C, second stage: 3 times at 144°C) to produced the stretched filaments.

In Comparative Example 1, conventional polyethylene having an intrinsic viscosity $[\eta]$ of 2.6 dl/g, an MFR of 0.11 g/10 min, a density of 0.956 g/cm^3, and a melting point of 131°C was extruded and stretched in the same manner as in Example 1, except that the extruder temperature was changed to 220°C. Thus, the stretched filaments were produced.

The physical properties of the resultant stretched filaments were determined according to the following methods.

The results were as shown in Table 1.

Density: ASTM D1505
Diameter: Micrometer
Tensile test: Tensile strength at break,

Young's modulus, and elongation (%) were determined at 23°C under the conditions of a stress rate of 200
mm/min and a chuck distance of 200 mm by using an Instron type universal testing machine CATY-1001ZS
manufactured by the Yonekura Co., Ltd.

Degree of orientation: Degree of orientation was calculated from the following equation by determining
the (110) face reflection by using X-ray diffraction apparatuses RU-200A and RU-200PL.

$$\text{Degree of orientation} = \frac{180 - \alpha°}{180}$$

wherein $\alpha°$ is the half width of (110) face reflection

Example 2 and Comparative Example 2

Stretchable strands of ultra-high-molecular-weight polyethylene having an outer diameter of 8.0 mm⌀
were produced in the same manner as in Example 1, except that a die having a length of 600 mm, an inner
diameter at die outlet of 12 mm⌀, an L/D ratio of 50, and an S_1/S_2 ratio of 1.9 was used, and that the screw
revolution number and the taking-off speed were changed to 50 rpm and 0.8 m/min, respectively. The
strands thus obtained were stretched at a draw ratio of 8 (i.e., first stage: 4 times at 134°C, second stage: 2
times at 145°C).

In Comparative Example 2, stretched filaments were produced in the same manner as in Example 2,
except that the conventional polyethylene used in Example 1 was used in lieu of the ultra-high-molecular-
weight polyethylene.

The physical properties of the resultant stretched filaments were determined in the same manner as in
Example 1. The results are as shown in Table 1.

Comparative Example 3

An attempt was made to produce stretchable strands of the ultra-high-molecular weight polyethylene
used in Example 1 in the same manner as in Example 1, except that a die having a length of 50 mm, an
inner diameter, at die outlet, of 6 mm⌀, an L/D ratio of 8.3, and an S_1/S_2 ratio of 1.1 was used, the setting
temperatures of the extruder, D_1, and D_2 were changed to 350°C, 230°C, and 140°C, respectively and
the screw revolution number and the taking-off speed were changed to 25 rpm and 0.7 m/min, respectively.
However, the polyethylene was intermittently cut off and continuous stretchable strands could not be
produced.

Table 1

Properties	Unit	Example 1 Million 240M	Comparative Example 1 Conventional polyethylene	Example 2 Million 240M	Comparative Example 2 Conventional polyethylene
Intrinsic viscosity [η]	dl/g	15.1	2.2	11.0	2.5
Density	g/cm^3	0.967		0.957	0.959
Diameter of product	mmφ	0.9		2.7	2.7
TS at break	MPa (kg/mm^2)	1078.7315(110)		441.3 (45)	274.6 (28)
Young's modulus	MPa (kg/mm^2)	9316.3175(950)		3726.5(380)	2056.4 (210)
Elongation	%	6		15	23
Degree of orientation	-	0.97		0.96	0.96

*: Stretching impossible due to filament breaking

Table 2

Properties	Unit	Example 3 — Million 240M						Comparative Example 4 — Conventional polyethylene				
		6 times 1 stage	8 times 1 stage	10 times 1 stage	10 times 2 stage	18 times 2 stage	30 times 2 stage	6 times 1 stage	8 times 1 stage	10 times 1 stage	12 times 2 stage	more than 18 times 2 stage
Inherent viscosity [η]	dl/g	14.8	14.8	14.8	14.8	14.8	14.8	2.3	2.3	Filament breaks*	2.3	Filament breaks*
Density	g/cm³	0.942	0.945	0.950	0.953	0.962	0.968	0.959	0.963	*	0.965	*
Diameter of product	mmφ	1.7	1.5	1.3	1.2	1.0	0.8	1.6	1.4	*	1.2	*
Tensile strength at break	kg/mm²	35	42	70	58	97	103	16	22	*	24	*
	MPa	343.2	411.9	686.5	568.8	951.2	1010.1	156.9	215.8	*	233.4	*
Young's modulus	kg/mm²	310	390	660	600	950	980	210	280	*	320	*
	MPa	3040.1	3824.6	6472.4	588.4	9316.3	9618.5	2059.4	2745.9	*	3138.1	*
Elongation	%	30	15	10	10	5	5	20	5	*	5	*
Folding return angle at 180°	degrees	110	15	3	5	3	3	85	60	*	25	*
at 90°	degrees	80	15	5	5	3	3	70	50	*	20	*

*: Stretching impossible

Example 3 and Comparative Example 4

The stretchable strands produced in Example 1 were stretched in a stretching bath containing triethylene glycol under the following draw ratios:

1) 6 times (i.e., first-stage stretching at 133°C)

2) 8 times (i.e., first-stage stretching at 133°C)

3) 10 times (i.e., first-stage stretching at 133°C)

4) 12 times (i.e., first stage: 6 times at 133°C, second stage: 2 times at 144°C)

5) 18 times (i.e., first stage: 6 times at 133°C, second stage: 3 times at 144°C)

6) 24 times (i.e., first stage: 6 times at 133°C, second stage: 3 times at 144°C)

In Comparative Example 4, conventional polyethylene having an intrinsic viscosity [η] of 2.6 dl/g, an MFR of 0.11 g/10 min, a melting point of 131°C, and a bulk density of 0.956 g/cm³ was used to produce stretched filaments in the same conditions as in Example 3, except that the extruder temperature was changed to 220°C.

The resultant stretched filaments were evaluated as follows:

Density: ASTM D 1505 (no annealing)

Diameter dimension: Same as in Example 1

Tensile test: Same as in Example 1

Folding return angle:

(1) Return angle after 10 minutes from a fold of 180° (see Fig. 2)

(2) Return angle after 10 minutes from a fold of 90° (see Fig. 3)

The results are as shown in Table 2.

As is clear from the results shown in Table 2, when the stretching ratio (or draw ratio) is 8 or more, more specifically, 10 or more, the desired plastic wires having a small return angle when folded and having an excellent tensile strength at break can be obtained. Contrary to this, when conventional polyethylene is used, the desired plastic wires having a small return angle when folded cannot be obtained.

Claims

1. An extruded stretched filament of ultra-high-molecular-weight polyethylene having an intrinsic viscosity [π] of at least 3.5 dl/g as determined in decalin solvent at 135°C, a tensile strength at break of at least 98.0665 MPa (10 kg/mm²), a draw ratio of at least 3, a C axis orientation degree of at least 0.9, and an outer diameter of 0.1 to 10 mm⌀.

2. A filament according to claim 1 wherein said intrinsic viscosity is at least 4 dl/g and the tensile strength at break is at least 196.133 MPa (20 kg/mm²).

3. An extruded stretched filament as claimed in claim 1, wherein said intrinsic viscosity is 6 to 20 dl/g, the tensile strength at break is 392.266 MPa (40 kg/mm²) or more, the draw ratio is 6 or more, the C axis orientation degree is 0.95 or more, and the outer diameter is 0.2 to 3 mm⌀.

4. A method for producing an extruded filament of ultra-high-molecular-weight polyethylene comprising the steps of:

melting the ultra-high-molecular-weight polyethylene in a screw extruder;

extruding the molten ultra-high-molecular-weight polyethylene from a die having an L/D ratio of at least 10 and an S_1/S_2 ratio of 1.0 to 5.0 where S_1 and S_2 are the respective cross-sectional areas of the inlet and outlet portions of the die;

taking-off the extrudate at a draft ratio of at least 1 while it is gradually cooled; and optionally stretching the extrudate.

5. An apparatus for producing an extruded filament of ultra-high-molecular-weight polyethylene comprising, in sequence in the machine direction:

an extruder provided with a grooved cylinder and a screw having a compression ratio of 1 to 2.5;

a die connected to the screw tip, said die having an L/D ratio of at least 10 and an S_1/S_2 ratio of 1.0 to 5.0 where S_1 and S_2 are the respective cross-sectional areas of the inlet and outlet portions of the die;

a gradual-cooling cylinder provided with an air ring or a sizing die at the inlet portion thereof for the extrudate; and

a taking-off unit.

6. A whitened wire obtainable by stretching a filament according to claim 2, the whitened wire having a folding return angle θ of 20° or less when folded at 90°C and 180°.

7. A whitened wire as claimed in claim 6, wherein the intrinsic viscosity [π] is 8 to 30 dl/g as determined in decalin solvent at 135°C, the tensile strength break is 490.3325 MPa (50 kg/mm²) or more, and the folding return angle θ when folded at 90° and 180° is 10° or less.

8. A method for producing a whitened wire according to claim 6 comprising producing an extruded filamend by a method according to claim 4 and stretching the filament at a draw ratio of 8 to 30.

9. A method as claimed in claim 8, wherein the filament is stretched at a draw ratio of 4 to 8 in a first stage and is stretched at a draw ratio of 2 to 5 in a second stage to form the wire at a total draw ratio of 8 to 30.

Revendications

1. Filament étiré extrudé en polyéthylène à poids moléculaire très élevé ayant une viscosité intrinsèque (π) d'au moins 3,5 dl/g telle que déterminée dans du solvant décaline à 135°C, une résistance à la traction à la rupture d'au moins 98,0665 MPa (10 kg/mm²), un taux d'étirage d'au moins 3, un degré d'orientation d'axe C d'au moins 0,9, et un diamètre extérieur de 0,1 à 10 mm.

2. Filament selon la revendication 1, dans lequel ladite viscosité intrinsèque est d'au moins 4 dl/g et la résistance à la traction à la rupture est d'au moins 196,133 MPa (20 kg/mm²).

3. Filament étiré extrudé selon la revendication 1, dans lequel ladite viscosité intrinsèque est de 6 à 20 dl/g, la résistance à la traction à la rupture est de 392,266 MPa (40 kg/mm²) ou plus, le taux d'étirage est de 6 ou plus, le degré d'orientation d'axe C est de 0,95 ou plus, et le diamètre extérieur est de 0,2 à 3 mm.

4. Procédé de fabrication d'un filament extrudé en polyéthylène à poids moléculaire très élevé comportant les étapes de :
   fusion du polyéthylène à poids moléculaire très élevé dans une extrudeuse à vis;
   extrusion du polyéthylène à poids moléculaire très élevé fondu dans une filière ayant un rapport L/D d'au moins 10 et un rapport S_1/S_2 de 1 à 5, où S_1 et S_2 sont les sections respectives des parties d'entrée et de sortie de la filière;
   évacuation du produit extrudé à un taux d'étirage d'au moins 1 alors qu'il est progressivement refroidi; et étirage éventuel du produit extrudé.

5. Dispositif de fabrication d'un filament extrudé en polyéthylène à poids moléculaire très élevé comportant, à la suite dans le sens de la machine :
   une extrudeuse pourvue d'un cylindre rainuré et d'une vis ayant un taux de compression de 1 à 2,5;
   une filière raccordée à la pointe de la vis, ladite filière ayant un rapport L/D d'au moins 10 et un rapport S_1/S_2 de 1 à 5, où S_1 et S_2 sont les sections respectives des parties d'entrée et de sortie de la filière;
   un cylindre de refroidissement progressif pourvu d'un anneau d'air ou d'une filière de calibrage au niveau de la partie d'entrée de celui-ci pour le produit extrudé; et
   une unité d'évacuation.

6. Fil blanchi pouvant être obtenu par étirage d'un filament selon la revendication 2, le fil blanchi ayant un angle de retour de pliage θ de 20° ou moins lorsqu'il est plié à 90° et 180°.

7. Fil blanchi selon la revendication 6, dans lequel la viscosité intrinsèque (π) est de 8 à 30 dl/g telle que déterminée dans du solvant décaline à 135°C, la résistance à la traction à la rupture est de 490,3325 MPa (50 kg/mm²) ou plus, et l'angle de retour de pliage θ lorsqu'il est plié à 90° et 180° est de 10° ou moins.

8. Procédé de fabrication d'un fil blanchi selon la revendication 6, comprenant la fabrication d'un filament extrudé au moyen d'un procédé selon la revendication 4 et l'étirage du filament à un taux d'étirage de 8 à 30.

9. Procédé selon la revendication 8, dans lequel le filament est étiré à un taux d'étirage de 4 à 8 dans une première phase et est étiré à un taux d'étirage de 2 à 5 dans une deuxième phase afin de former le fil avec un taux d'étirage total de 8 à 30.

Patentansprüche

1. Extrudierter gestreckter Faden aus Polyethylen von ultrahohem Molekulargewicht mit einer Grenzviskositätszahl [π] von mindestens 3,5 dl/g, bestimmt in Dekalin als Lösungsmittel bei 135°C, einer Reißfestigkeit bei Bruch von mindestens 98,0665 MPa (10 kg/mm²), einem Verstreckverhältnis von mindestens 3, einem Orientierungsgrad in C-Achsen-Richtung von mindestens 0,9 und einem Außendurchmesser von 0,1 bis 10 mm⌀.

2. Faden nach Anspruch 1, bei dem die Grenzviskositätszahl mindestens 4 dl/g und die Reißfestigkeit bei Bruch mindestens 196,133 MPa (20 kg/mm²) beträgt.

3. Extrudierter gestreckter Faden nach Anspruch 1, bei dem die Grenzviskositätszahl 6 bis 20 dl/g, die Reißfestigkeit bei Bruch 392,266 MPa (40 kg/mm²) oder größer, das Verstreckverhältnis 6 oder größer, der Orientierungsgrad in Richtung der C-Achse 0,95 oder größer, und der Außendurchmesser 0,2 bis 3 mm⌀ ist.

4. Verfahren zur Herstellung eines extrudierten Fadens aus Polyethylen von ultrahohem Molekulargewicht, folgende Schritte aufweisend:
   Schmelzen des Polyethylens von ultrahohem Molukulargewicht in einer Schneckenstrangpresse;
   Extrudieren des geschmolzenen Polyethylens von ultrahohem Molekulargewicht aus einer Form mit einem L/D-Verhältnis von mindestens 10 und einem S_1/S_2-Verhältnis von 1,0 bis 5,0, wobei S_1 und S_2 die jeweiligen Querschnittsflächen der Einlaß- und Auslaß-Bereiche der Form sind;
   Entfernen des Extrudats bei einem Neigungsverhältnis von mindestens 1 während es allmählich gekühlt wird; und wahlweise Strecken des Extrudats.

5. Vorrichtung zur Herstellung eines extrudierten Fadens aus Polyethylen von ultrahohem Molekulargewicht, in Arbeitsrichtung in Folge aufweisend:
   einen mit einem ausgekehlten Zylinder und einer Schnecke mit einem Kompressionsverhältnis von 1 bis 2,5 ausgestatteten Extruder;
   eine mit der Schneckenspitze verbundene Form, die ein L/D-Verhältnis von mindestens 10 und ein S_1/S_2-Verhältnis von 1,0 bis 5,0 besitzt, wobei S_1 und S_2 die jeweiligen Querschnittsflächen der Einlaß- und Auslaß-Bereiche der Form sind;
   einen Zylinder für allmähliches Kühlen, der an seinem Einlaßbereich für das Extrudat mit einem Luftring oder einer Abmessungskontrollform ausgestattet ist; und
   eine Entfernungs-Einheit.

6. Gebleichter Draht, erhältlich durch Strecken eines Fadens nach Anspruch 2, wobei der gebleichte Draht einen Knick-Rückkehrwinkel θ von 20° oder weniger hat, wenn er bei 90°C und 180° geknickt wird.

7. Gebleichter Draht nach Anspruch 6, bei dem die Grenzviskositätszahl [π] 8 bis 30 dl/g, bestimmt in Dekalin als Lösungsmittel bei 135°C, die Reißfestigkeit bei Bruch 490,3325 MPa (50 kg/mm²) oder größer und der Knick-Rückkehrwinkel θ, wenn er bei 90° und 180° geknickt wird, 10° oder weniger ist.

8. Verfahren zur Herstellung eines gebleichten Drahts nach Anspruch 6, beinhaltend das Herstellen eines extrudierten Fadens nach einem Verfahren nach Anspruch 4 und Strecken des Fadens bei einem Verstreckverhältnis von 8 bis 30.

9. Verfahren nach Anspruch 8, bei dem der Faden in einer ersten Stufe bei einem Verstreckverhältnis von 4 bis 8 gestreckt wird und in einer zweiten Stufe bei einem Verstreckverhältnis von 2 bis 5 gestreckt wird, um den Draht bei einem Gesamtverstreckungsverhältnis von 8 bis 30 zu bilden.
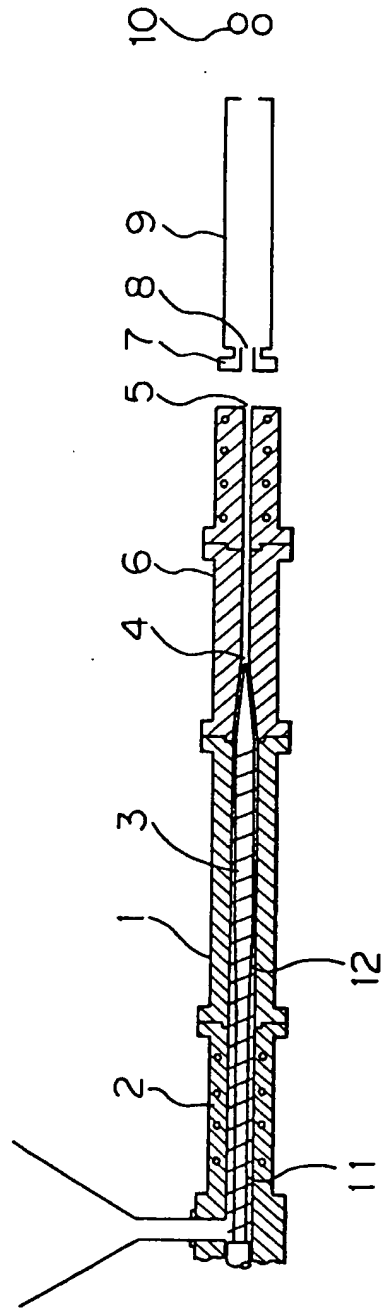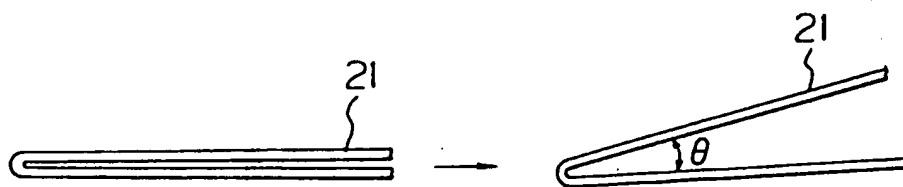
Fig. I

Fig. 2(a)   Fig. 2(b)

Fig. 3(a)   Fig. 3(b)